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PATENT SPECIFICATION

NO DRAWINGS

828,231

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International Classification:—C07c. D06m.

COMPLETE SPECIFICATION

Improvements relating to Insecticidal Compounds and their use

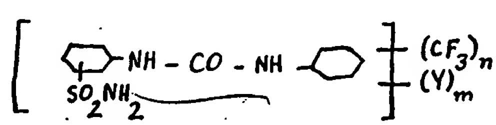
We, J. R. GEIGY A.—G., a body corporate organised according to the laws of Switzerland, of 215 Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns insecticidal agents, processes for the production thereof and their use for the protection of keratine material against destruction caused by injurious insects. The invention also concerns, as industrial product, the material protected by these agents from destruction caused by injurious insects.

Various processes concerning the production of sulphonated insecticidal agents are already known. However, compounds with sulphonic acid groups only draw completely onto keratine material, for example, wool, from a relatively strongly acid bath. Insecticidal agents are often applied in the dyebath when dyeing the wool. When dyestuffs needing only a slight amount of acid or having slight migratory power are used, such as for example complex heavy metal compounds of monoazo dyestuffs having no acid dissociating groups, the presence of acid in the dyebath has an adverse effect on the evenness of the wool dyeing. There is, therefore, a need for insecticidal agents which draw onto wool from a neutral to weakly acid dyebath and can, therefore, be applied with complex heavy metal compounds of unsulphonated azo dyestuffs. Thus, protective agents against injurious insects which have sufficient drawing power from a neutral bath are a valuable contribution to the art.

In this connection, the treatment of keratine material with insecticidal agents which have no sulphonic acid groups and are insoluble in water has already been suggested. This was done by using aqueous emulsions of such agents in the preparation of the dyebaths. However, it is difficult to make such emulsions durable and often undesirable precipitates occur in the dyebath.

It has now been found that water soluble compounds having no sulphonic acid groups, which compounds have good activity against insects that are injurious to keratine fibres, are obtained if an isocyanate of the aromatic series is reacted with an aromatic amine, the components being so chosen that an H_2N — SO_2 —group is introduced with the aromatic amine and at least two substituents selected from aromatically bound halogen atoms or trifluoromethyl groups are present in the reaction product, which corresponds with the formula:



wherein Y represents a halogen atom
n represents an integer from 0 — 2 and
m represents an integer from 0 — 5
and wherein n + m are at least 2.

For technical and economical reasons, chiefly chlorine is meant by halogen atoms, however, the corresponding derivatives substituted by bromine, fluorine and iodine can also be used.

The insecticidal compounds produced according to the present invention are new. Their production by reacting isocyanates of the aromatic series with the aromatic amino compounds occurs under conditions which are usual for such reactions which are known per se.

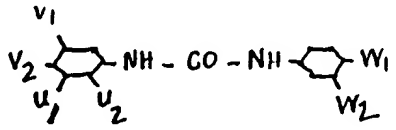
4 - Chlorophenyl isocyanate, 3.4 - dichlorophenyl isocyanate, 3.4.5 - trichlorophenyl isocyanate, 3 - trifluoro - methylphenyl isocyanate, 3 - trifluoromethyl - 4 - chlorophenyl isocyanate and 3 - chloro - 4 - trifluoromethylphenyl isocyanate can be used as aromatic isocyanates.

Examples of aromatic amines which can be

used are 2- or 3- or 4-aminobenzene sulphonic acid amide, 3-amino-4-chloro or 2-chloro-5-aminobenzene sulphonic acid amide, 2.3-dichloro-5-amino- or 2-amino-4.5-dichlorobenzene sulphonic acid amide, and in addition 2-trifluoromethyl-4-aminobenzene sulphonic acid amide and 2-amino-4-trifluoromethyl-5-chlorobenzene sulphonic acid amide.

As valuable compounds which can be used according to the present invention chiefly those can be named in which at least one aromatic radical is substituted in two positions by halogen atoms and/or trifluoromethyl groups, this substitution advantageously being by halogen and trifluoro methyl substituents in the *p*- and *m*-positions to the urea bridging member. Particularly active are those derivatives in which the $H_2N—SO_2—$ group is in the *m*- or preferably in the *o*-position to the —NH—CO—NH group.

Thus the most valuable compounds correspond with the general formula:



wherein one U represents — SO_2NH_2
the other U represents hydrogen
one V represents chlorine or the trifluoromethyl group,
the other V represents hydrogen or chlorine
one W represents chlorine or the trifluoromethyl group, and
the other W represents chlorine.

The activity of such compounds containing the $H_2N—SO_2—$group could not have been foreseen, as if known sulphonated insecticidal agents are converted into the corresponding $H_2N—SO_2—$ derivatives by modification of their sulphonic acid group the insecticidal action is reduced to a great extent. Thus for example, 2.2^1 - dihydroxy - $3.3^1.5.5^1$ - 4^{11} - pentachloro - triphenyl methane - 2^{11} - sulphonic acid amide has not sufficient insecticidal activity for practical purposes when compared with the corresponding sulphonic acid.

The new compounds according to the present invention, however, have remarkable insecticidal activity and can be used in particular for the protection of keratine material against injurious pests such as the larvae of moths, fur and carpet beetles. In the form of their alkali metal salts, e.g. the lithium, sodium and potassium salts, they have sufficient water solubility to be applied to keratine material from such solutions. When applied during the dyeing process the compounds draw onto keratine material, e.g. wool, completely from a neutral to weakly acid bath and they are fast to washing and rubbing. As has already been explained, such insecticidal agents are very advantageous as they can be used in the same dyebath with dyestuffs which draw from a neutral to weakly acid medium. However, the new compounds can not only be applied in aqueous solutions. Those which are soluble in organic solvents can also be used in this form for the impregnation of keratine material. Finally, the compounds can also be used in the form of dispersions or in powder form, possibly with carriers, as insecticidal agents.

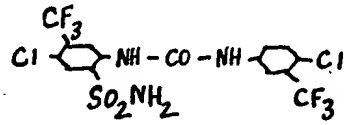
The following examples serve to illustrate the invention. Where not otherwise stated, the temperatures are in degrees Centigrade and the parts are given as parts by weight. The relationship of parts by volume to parts by weight is as that of litres to kilogrammes.

Example 1

27.4 Parts of 2 - amino - 4 - trifluoromethyl - 5 - chlorobenzene sulphonic acid amide are dissolved at 50—55° in 250 parts of abs. butanone. A solution of 22.1 parts of 3 - trifluoromethyl - 4 - chlorophenyl isocyanate in 220 parts of abs. nitrobenzene is added and the mixture is heated for 16 hours at 40—45° while stirring.

The butanone is then distilled off and, after cooling, 200 parts of chlorobenzene are added to the residue. The precipitate which forms is filtered off, washed with chlorobenzene and dried in a vacuum at 100°.

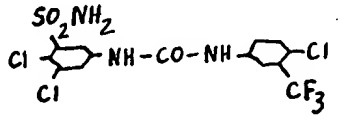
After crystallisation from alcohol, the compound melts at 208—210°. It corresponds to the formula:



Nitrogen determination: found 8.3% N
calculated 8.4% N

Example 2

24.1 Parts of 2.3 - dichloro - 5 - aminobenzene sulphonic acid amide and 22.1 parts of 3 - trifluoromethyl - 4 - chlorophenyl isocyanate are reacted as described in Example 1. A white body which melts at 235—237° is obtained. It corresponds to the formula:



Analysis: found 9.0% N
calculated 8.9% N

Example 3

24.1 Parts of 2.3 - dichloro - 5 - aminobenzene sulphonic acid amide and 18.8 parts of 3.4 - dichlorophenyl isocyanate are reacted

as described in the process of Example 1. The compound obtained melts at 239—240° and corresponds to the formula:

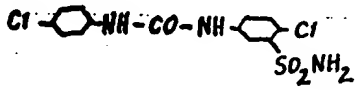
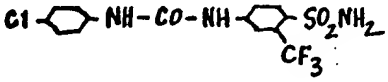
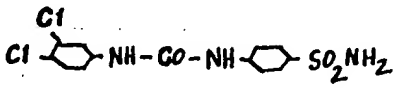
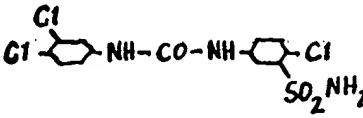
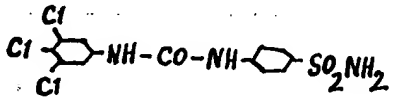
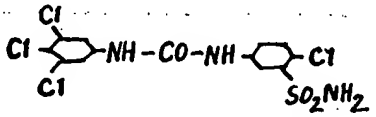
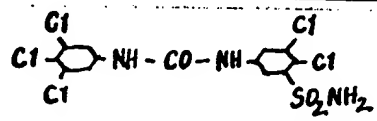
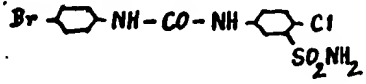
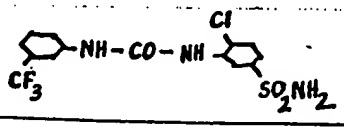
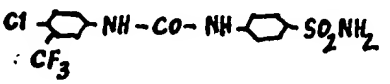
Analysis: found 9.8% N
calculated 9.8% N

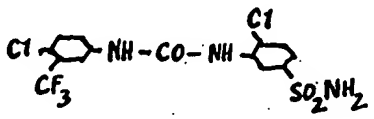
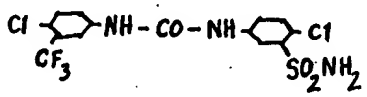
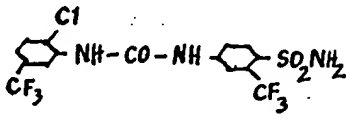
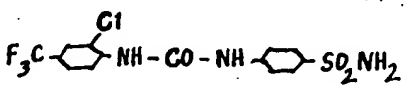
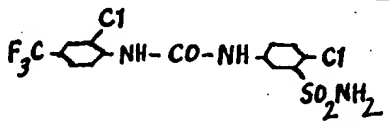
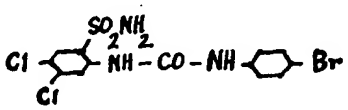
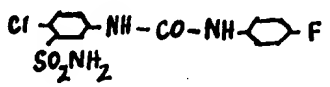
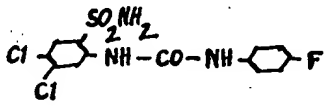
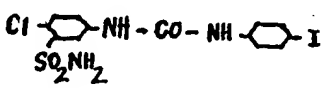
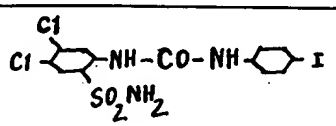
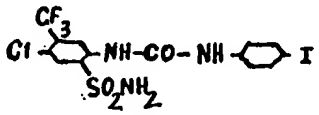
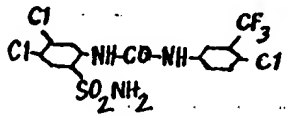
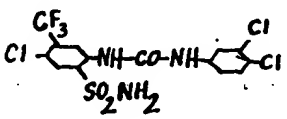
EXAMPLE 4

0.2 Parts of the compound according to Example 2 are dissolved with dilute caustic soda lye and the solution is brought up to 1000 parts by volume with water. 20 Parts of wool are treated in this solution for 30 minutes at 50°.

After rinsing, wringing out and drying, the wool is resistant to attack by the larvae of Tineola bis., Anthrenus vorax and Attagenus piceus.

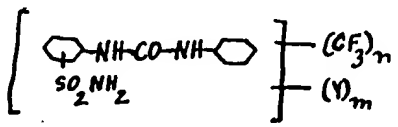
The following compounds can be produced in a manner analogous to those described in the above examples:

No.		M. P.
1		251—252°
2		217—219°
3		260—262°
4		253—255°
5		276—278°
6		280—283°
7		282—285°
8		258—262°
9		218—220°
10		243—245°

No.		M. P.
11		233—235°
12		240—242°
13		224—226°
14		226—228°
15		231—233°
16		238°
17		214°
18		259°
19		239°
20		227°
21		183°
22		210—211°
23		193—195°

WHAT WE CLAIM IS:—

1. A compound having the formula:



wherein

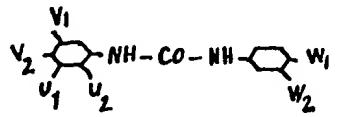
Y represents halogen,

n represents an integer from 0 — 2,

m represents an integer from 0 — 5

and wherein n + m are at least 2.

2. A compound having the formula:



wherein one U represents $-SO_2NH_2$,

the other U represents hydrogen,

one V represents chlorine or the trifluoromethyl group,

the other V represents hydrogen or chlorine and

one W represents chlorine or the trifluoromethyl group and

the other W represents chlorine

3. Process for the production of water soluble insecticidal compounds characterised by reacting an isocyanate of the aromatic series with an aromatic amine, the components being so chosen that an H_2N-SO_2 group and at least two substituents selected from aromatically bound halogen atoms or trifluoromethyl groups are present in the reaction product, the H_2N-SO_2 group being introduced with the aromatic amine.

4. Manufacture of compounds substantially as described with reference to any of the foregoing examples 1 to 3.

5 Compounds whenever prepared or produced by the processes of manufacture particularly described.

6. A compound as specified in any of the foregoing examples 1 to 3 or in the Table.

7. Process for the protection of material containing keratin fibres characterised by the use of any of the compounds as hereinbefore claimed by a process substantially as described in example 4.

8. Materials containing keratin fibres protectively treated with any of the compounds defined in claim 1.

9. Manufacture of agents containing insecticidal compounds for treating keratin fibres in an aqueous medium substantially as hereinbefore described.

10. Agents containing insecticidal compounds for treating keratin fibres in an aqueous medium whenever produced as claimed in claim 9.

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Chartered Patent Agents,
329 High Holborn, London, W.C.1.

Reference has been directed, in pursuance of Section 8 of the Patents Act, 1949, to Specification No. 753,171.

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